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***In situ* Raman Spectroscopy of COOH-functionalized SWCNTs Trapped with Optoelectronic Tweezers**

Peter J. Pauzauskie^{1†}, Arash Jamshidi², Joseph M. Zaug¹, Sarah Baker¹,
T.Y.-J. Han¹, Joe H. Satcher, Jr.¹, and Ming C. Wu^{2†}

1 – Chemical Sciences Division, Lawrence Livermore National Laboratory, 7000 East Ave.

L-231, Livermore, CA 94551

2 – Department of Electrical Engineering, University of California, Berkeley, Berkeley, CA 94720

† To whom correspondence should be addressed: peterpz@uw.edu

** Present address: Department of Materials Science & Engineering, University of Washington, Seattle, WA 98195*

Abstract:

Optoelectronic tweezers (OET) are used to trap and deposit aqueous dispersions of carboxylic-acid functionalized single-walled carbon nanotube bundles. Dark-field video microscopy is used to visualize the dynamics of the bundles both with and without virtual electrodes, showing rapid accumulation of carbon nanotubes when optical virtual electrodes are actuated. Raman microscopy is used to probe SWCNT materials following deposition onto metallic fiducial markers as well as during trapping. The local carbon nanotube concentration is observed to increase rapidly during trapping by more than an order of magnitude in less than one second due to localized optical dielectrophoresis forces. This combination of enrichment and spectroscopy with a single laser spot suggests a broad range of applications in physical, chemical, and biological sciences.

Introduction:

One persistent challenge in molecular sensing is the enriching of candidate analytes to concentrations high enough for detection. Optoelectronic tweezers (OET) recently have been used as a versatile platform for trapping objects such as polystyrene spheres, living cells¹, and solid-state nanowires², using 100,000x less optical power than single-beam laser traps. Based on a combination of dielectrophoresis and optical image patterning, OET has the unique capability of massively parallel localization of organic and inorganic nanoscale structures for both direct visualization and spectroscopic characterization. In this report we use carboxylic-acid (COOH-) functionalized single-walled carbon nanotubes as a system to demonstrate analyte enrichment by over an order of magnitude with a low-power OET trapping laser that serves simultaneously as a Raman spectroscopic probe.

COOH-functionalized carbon nanotubes have been used as a surfactant-free alternative for aqueous SWCNT suspensions, with the hydrophilic COOH-surface functional groups serving as a means to suspend the nanotubes on polar solvents such as water³. In this work, COOH-functionalized SWCNTs (P3, Carbon Solutions, Inc., ~4 atomic % COOH-functionalization) are dispersed as-made in Milli-Q deionized water, bath-sonicated for 30 min, and centrifuged for 30 min at 16,000 g to remove large

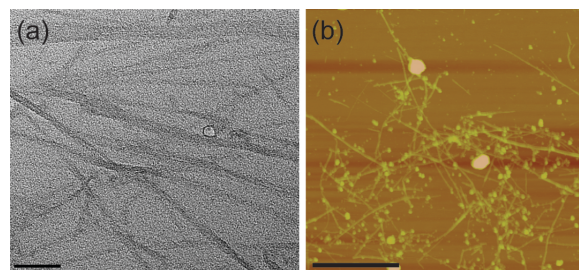


Figure 1. Characterization of COOH-functionalized SWCNTs used in this study (a) Bright field transmission electron micrograph. Scale bar = 50 nm. (b) Atomic force micrograph of SWCNTs on an aminopropylsilane coated mica wafer. Scale bar = 1 μ m.

bundles and other metallic catalyst particles yielding a semitransparent solution. Transmission electron microscopy and atomic force microscopy are used to characterize the physical dimensions for the nanotube bundles, with diameters ranging from 2 to 11 nm, and lengths ranging from 0.1 to 2 μ m (Fig. 1a,b), with a mean bundle diameter of 6.4 \pm 2.4 nm. We assume the bundles consist of a mixture of semiconducting and metallic tubes, with the dielectric properties of the metallic tubes dominating the overall dielectric response of the bundles.

OET chambers are fabricated as reported previously¹. Dark-field optical microscopy is used⁴ to image aqueous suspensions of SWCNT bundles with a video-rate EMCCD (Andor, iXon). When a 15Vpp, 100kHz trapping voltage is applied across the

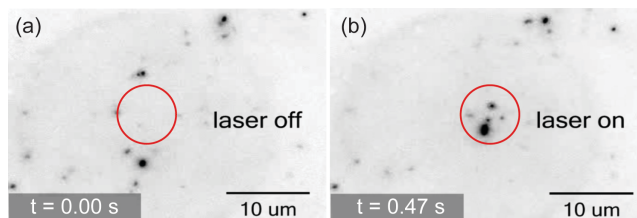


Figure 2. Dark-field EMCCD video microscopy of optoelectronic trapping of COOH-SWCNTs with laser off (a) and on (b) at an AC bias of 15Vpp, 100kHz. Images are inverted to enhance visibility of faint light scattering from SWCNT bundles. The laser line (Ar⁺, 488 nm) is blocked by a holographic notch filter.

OET chamber the SWCNTs are observed to move away from one another (Fig. 2a) due to repulsive, in-phase dipole-dipole

interactions. When the trapping laser is turned on (488 nm, 100 μ W) SWCNT bundles are observed to migrate into the laser spot (Fig. 2b), agreeing with previous reports of positive dielectrophoresis forces for metallic SWCNTs⁵.

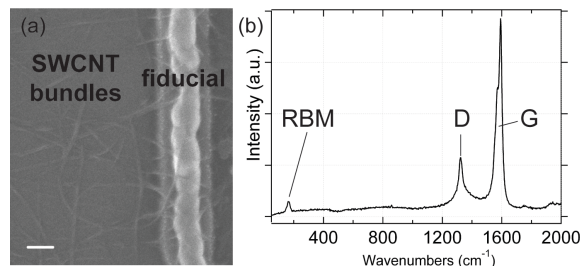


Figure 3. *ex situ* characterization of COOH-SWCNTs following deposition with optoelectronic tweezers at high peak-to-peak voltages. (a) SEM image of SWCNT bundles deposited next to a Ti/Au fiducial marker. Scale bar = 100 nm. (b) Raman spectrum of deposited SWCNT bundles showing radial breathing mode (RBM), D, and G bands; a-Si background subtracted.

At high trapping voltages (20 Vpp, 100kHz) the SWCNTs are observed to attach irreversibly to the a-Si surface. Electron beam lithography is used to pattern a grid of metallic fiducial markers (20 nm Ti, 50 nm Au) on top of the polished a-Si layer, which are then used to locate regions on the OET surface following Raman deposition experiments. Using scanning electron microscopy (SEM) (Fig. 3a) and micro-Raman (Fig. 3b) for *ex situ* characterization confirms that the deposited structures are indeed SWCNT bundles.

Single beam laser tweezers have been used previously for three-dimensional trapping^{6, 7}, and Raman characterization⁸ of SWCNT suspensions, however, they typically require several milliwatts of power to produce electric field gradients sufficient for trapping. Confocal micro-Raman measurements may also be performed with OET in an upright backscattering configuration. Generally, several hundred μ W from the polarized 632.8 nm line of a CW He:Ne laser (Fig. 4a) are focused to an area of $\sim 75 \mu\text{m}^2$, yielding a maximum local irradiance of $<500 \text{ W/cm}^2$, which is more than sufficient to actuate the OET virtual trapping electrodes while simultaneously providing enough inelastically scattered photons for Raman spectroscopy. The focal point is positioned in the chamber with a motorized translation stage, using the Raman signal of the a-Si as a means of ensuring that the Raman focal volume coincides directly with the OET-trapping volume.

When Raman spectra are taken from the COOH-SWCNT dispersions, signal levels are low due to both the low concentration of tubes in solution as well as defects within the carbon lattice that decrease the inelastic scattering cross section⁹. Raman spectra are acquired both with and without the OET trapping voltage (6 Vpp, 100 kHz) at both the a-Si/fluid interface (Fig. 4a) and $\sim 20 \mu\text{m}$ above the a-Si. Once the trapping voltage is applied the in-plane E_{2g} stretching mode at 1591 cm^{-1} collected from the a-Si/fluid interface shows an 18-fold increase based on a ratio of integrated 1591 cm^{-1} peak areas. The enhancement exists both when compared to the case with the trapping voltage off, and with the voltage on, but with the focus $\sim 20 \mu\text{m}$ above the a-Si surface (Fig. 4b). The signal enhancement is reversible, depending only on whether the laser is present to generate inhomogeneous lateral electric trapping fields. When the AC-field is turned off, the signal relaxes to the background level,

suggesting that trapped SWCNTs become free to diffuse through solution in agreement with dark-field images (Fig. 2).

In conclusion, we report here the first demonstration of simultaneous trapping and micro-Raman spectroscopy of SWCNT materials with OET, providing a versatile means for locally concentrating dilute samples, therefore, enhancing the

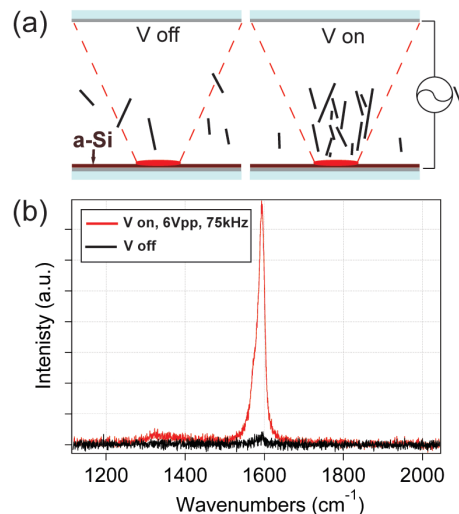


Figure 4. Enhanced Raman signal from COOH-SWCNTs trapped with OET (a) Schematic of micro-Raman experiment (b) Raman spectrum (480 W/cm^2 , 60s) with (red) and without (black) OET trapping bias of 6Vpp, 75kHz.

detected Raman signals by over an order of magnitude. This signal enrichment can potentially be combined with other Raman enhancement techniques such as surface-enhanced Raman spectroscopy (SERS) to create more sensitive Raman probes. OET is unique in that a few hundred micro-Watt laser intensities can be used to enrich the local analyte concentration while simultaneously producing inelastically scattered photons for sample characterization. This combination of enrichment and spectroscopy with a single laser spot suggests a broad range of applications in physical, chemical, and biological sciences. Finally, these results will help guide future experiments with isolated single-walled carbon nanotubes.

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